

1,071,298



PATENT SPECIFICATION

NO DRAWINGS

1,071,298

Date of Application and filing Complete Specification: Aug. 13, 1964.
No. 33007/64.

Application made in United States of America (No. 301,875) on Aug. 13, 1963.

Application made in United States of America (No. 312,002) on Sept. 27, 1963

Application made in United States of America (No. 337,997) on Jan. 16, 1964.

Application made in United States of America (No. 356,639) on April 1, 1964.

Application made in United States of America (No. 384,780) on July 23, 1964.

Complete Specification Published: June 7, 1967.

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PATENTS ACT, 1949

SPECIFICATION NO. 1,071,298

Reference has been directed, in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to Patent Nos. 993,596, 1,017,444 and 1,042,892.

THE PATENT OFFICE,
10th November 1967

D 94181/4

Improvements in or relating to Polyfunctional Compounds and Polymers Modified with said Compounds

We, J. P. STEVENS & Co. INC., a corporation organized under the laws of the State of Delaware, United States of America, of 1460 Broadway, New York, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention relates to novel polyfunctional compounds, and more particularly, nitrogen-containing polyfunctional compounds which can be employed for a wide variety of purposes such as crosslinking agents for polymers, as therapeutic agents, and as monomers for the preparation of new polymeric materials.

10 The novel polyfunctional compounds of the present invention are characterized by the presence of at least two functional groups which are capable of reacting with the active hydrogen atoms of various polymeric materials as well as acting as sites for polymerization and as centers of therapeutic activity.

15 Accordingly, it is an object of this invention to provide a new and novel class of nitrogen-containing polyfunctional compounds which contain two particular terminal groups capable of acting as reactive sites.

It is a still further object of this invention to provide a novel class of polyfunctional amide compounds.

20 It is a further object of the present invention to provide a method for the chemical modification of polymers containing active hydrogen atoms whereby desirable properties are introduced into the polymer.

It is a further object of the present invention to provide a method for crosslinking cellulosic textile materials, such as cellulosic fabrics, in order to impart desirable properties thereto.

25 It is a further object of the present invention to provide crosslinked polymers that are characterized by desirable physico-chemical properties.

It is a further object of the present invention to provide crosslinked cellulosic textiles having improved dimensional stability, crease recovery and flat drying properties.

30 In attaining the above objects, one feature of the invention resides in compounds which have two terminal activating groups present in the molecule and which are derived from cyclic or acyclic bis-secondary amines.

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Index at acceptance:—C2 C(1F4C4, 1F4C6, 1F4D1, 1F4F5, 2B21, 2B53A3, 2B53C3, 2B53G, 2B53J2, 2D25, 2D43A, 2D43E, 2D43F, 2D43S1, 2D43S4, 3A8A4, 3A8B2, 3A8C6, 3A8K, 3A12A4A, 3A12B6, 3A12C4, 3A12C5, 3A12C6, 3A14B3D, 3A14B8A, 3C6, 3C7); C3 P(4D1A, 4K8, 4K11, 4T2A); C3 U(2B, 2C, 2D, 2E, 4, 5); D1 P(A1, B2A2, B2B1, B2B2, C2A12A10, C2A12B4, C2C2, C2C4, C2C5, C2C7, C2C9, C2C10, C2C16)

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COMPLETE SPECIFICATION

Improvements in or relating to Polyfunctional Compounds and Polymers Modified with said Compounds

We, J. P. STEVENS & CO. INC., a corporation organized under the laws of the State of Delaware, United States of America, of 1460 Broadway, New York, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention relates to novel polyfunctional compounds, and more particularly, nitrogen-containing polyfunctional compounds which can be employed for a wide variety of purposes such as crosslinking agents for polymers, as therapeutic agents, and as monomers for the preparation of new polymeric materials.

10 The novel polyfunctional compounds of the present invention are characterized by the presence of at least two functional groups which are capable of reacting with the active hydrogen atoms of various polymeric materials as well as acting as sites for polymerization and as centers of therapeutic activity.

15 Accordingly, it is an object of this invention to provide a new and novel class of nitrogen-containing polyfunctional compounds which contain two particular terminal groups capable of acting as reactive sites.

It is a still further object of this invention to provide a novel class of polyfunctional amide compounds.

20 It is a further object of the present invention to provide a method for the chemical modification of polymers containing active hydrogen atoms whereby desirable properties are introduced into the polymer.

It is a further object of the present invention to provide a method for crosslinking cellulosic textile materials, such as cellulosic fabrics, in order to impart desirable properties thereto.

25 It is a further object of the present invention to provide crosslinked polymers that are characterized by desirable physico-chemical properties.

It is a further object of the present invention to provide crosslinked cellulosic textiles having improved dimensional stability, crease recovery and flat drying properties.

30 In attaining the above objects, one feature of the invention resides in compounds which have two terminal activating groups present in the molecule and which are derived from cyclic or acyclic bis-secondary amines.

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Another feature of the present invention resides in compounds which have two terminal organic activating groups present in the molecule, which compounds also contain a polyvalent nitrogen-containing radical which is a hydrazinyl derivative.

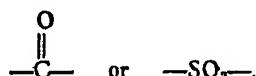
5 A further feature of the present invention resides in the method of imparting desirable properties to polymers containing active hydrogen atoms, particularly cellulose textile materials, by applying thereto novel compounds referred to above and reacting the compounds with the aforesaid polymers in the presence of a suitable catalyst to produce a crosslinked polymeric material.

.10 A still further feature of the present invention resides in the crosslinked polymers, particularly crosslinked cellulose textile materials, produced by the aforementioned methods and which possess desirable properties.

10 The polyfunctional nitrogen-containing compounds of this invention contain two terminal groups represented by the structural formula:



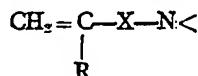
15 15 wherein Z is an organic reactive group as defined hereinafter, X is



The functional terminal group $Z-X-N<$ can be directly joined to another terminal group by a nitrogen-to-nitrogen bond or two terminal groups of the above formula can be joined by organic radicals.

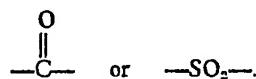
20 20 Included among the compounds of the present invention are those which contain two of the same or different terminal groups represented by the structure I, II or III.

I.



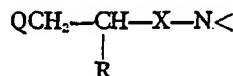
in which R is hydrogen or an alkyl group containing from 1 to 5 carbon atoms, and X is

25



25

II.

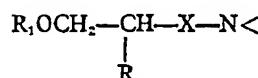


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in which R and X have the meaning as defined above, and Q is (a) the radical corresponding to a conjugate base of a Lowry-Brensted acid which has a dissociation constant in water between 5×10^{-2} and 5×10^{-4} , or (b) the residue of a tertiary ammonium cation, and

30

III.

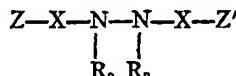


in which R and X have the meaning as defined above and R_1 is hydrogen or an alkyl group containing from 1 to 5 carbon atoms.

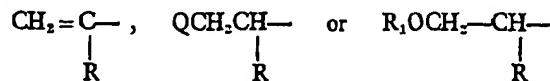
35 Compounds which come within the scope of this invention containing terminal functional groupings represented by the formulae I, II and III directly linked together by nitrogen-to-nitrogen bonds are derived from hydrazine and are represented by the structural formula:

35

IV.

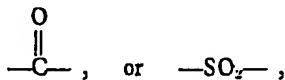


wherein Z and Z', the organic reactive groups, are each:



wherein R and R₁ are hydrogen or an alkyl group containing from 1 to 5 carbon atoms and

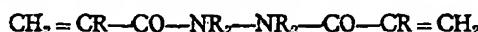
5 X is



Q has the meaning defined above and
R₂ is hydrogen or an alkyl group containing from 1 to 5 carbon atoms or a hydroxymethyl group. A particularly suitable group of such polyfunctional nitrogen-containing compounds are those having the general formula

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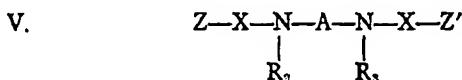
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wherein R and R₂ have the same meaning as above.

Further included in this invention are compounds derived from acyclic bis-secondary amines wherein functional terminal groups are linked together by a divalent organic radical and represented by the structural formula:

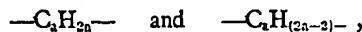
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wherein X, Z and Z' have the meanings as defined above, R₃ is an alkyl group containing from 1 to 5 carbon atoms, and

20 A is a divalent acyclic aliphatic organic radical containing at least 3 carbon atoms, including the alkylene group and alkenylene groups of the formulae:

20



respectively, where a is an integer of from 3 to 10.

Further examples of —A— include:

25 polyoxyethylene radicals of the formula
—(C₂H₄O)_mC₂H₄ wherein m is from 1 to 20;

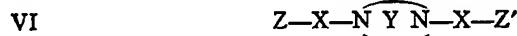
25

polyoxypropylene groups of the formula
—(C₃H₆O)_mC₃H₆— wherein m is 1 to 20;

hydroxyalkylene groups of the formula
C_nH_{2n-x}(OH)_x wherein n is 3 to 10 and x is 1 to 4.

30 Compounds of this invention, which are derived from cyclic bis-secondary diamines and where the terminal functional groupings are linked by a divalent organic group, are represented by the generic structural formula:

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in which X, Z and Z' have the meanings as defined above but when Z is

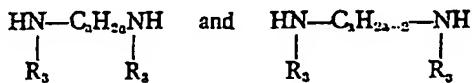
35 $\text{R}_1\text{OCH}_2\underset{\text{R}}{\text{—CH—}}$

35

then Z' is either $\text{CH}_2=\underset{\text{R}}{\text{C}}—$ or $\text{Q} \cdot \text{CH}_2 \cdot \underset{\text{R}}{\text{CH}}—$, and the symbols $\overbrace{\text{N Y N}}{\text{—}}$ as used
herein represents the residue of a cyclic bis-secondary amine.

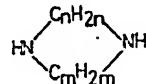
It is to be noted that the compounds coming with the scope of formulae V and VI contain nitrogen atoms which are free of hydrogen atoms.

Examples of suitable acyclic bis-secondary diamines, both saturated and unsaturated, which can be employed to produce the novel compounds of the present invention of formula V above may be represented by the generic formulae:



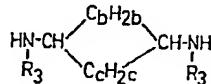
in which R_3 is a lower alkyl group, and a is an integer with a value of from 3 to 10.

Coming within the scope of the suitable cyclic diamines which may be employed to produce the novel compounds of this invention of formula VI above are alkyl-substituted piperazines and unsubstituted piperazines, pyrazolidines, and the like, which may be represented by the structural formula:



in which n and m each have a value of 0 to 4, and preferably of 1 to 4, the sum of n and m being at least two.

Further cyclic bis-secondary diamines which may be employed to produce the novel compounds of the invention are alkylamino cycloalkanes such as 1,4 bis(methylamino) cyclohexane represented by the structural formula:



wherein R_3 is an alkyl group containing from 1 to 5 carbon atoms and b and c are integers with a value of 1 to 2.

The radical Q which forms a part of the terminal grouping of formula II above is the radical corresponding to a conjugate base of a Lowry-Brønsted acid and which has a dissociation constant in water between 5×10^{-2} and 5×10^{-5} or the residue of a tertiary ammonium cation. Included within the scope of this definition are polar residues derived from weakly nucleophilic reagents. Illustrative of but not limiting the polar residues are the following:

| | | | |
|----|--------------------------|---|----|
| | Sulfate | $-\text{OSO}_3\text{M}$ | |
| | Thiosulfate | $-\text{SSO}_3\text{M}$ | |
| | Acetate | $-\text{OCOCH}_3$ | |
| 30 | Formate | $-\text{OCOH}$ | 30 |
| | Propionate | $-\text{OCOC}_2\text{H}_5$ | |
| | Pyridinium | NC_5H_5^+ | |
| | Benzylidemethyl Ammonium | $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \qquad \diagdown \\ \text{H} \quad \text{C}_6\text{H}_5 \\ \diagup \quad \\ -\text{NCH}_2\text{C}_6\text{H}_5 \end{array}$ | |

35 wherein M is an alkali metal, e.g., Na, K, Li, or ammonium.

Among the compounds of the present invention are those containing terminal groupings of formulae I, II and III wherein X is O . These compounds can be



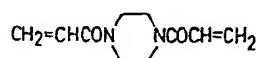
5 prepared from available raw materials in an economical manner. Because of their excellent water solubility and high reactivity, they are particularly suitable as cross-linking agents for polymeric materials containing active hydrogen atoms, as determined by the Zerewitinov method. For example, the compounds of the present invention, particularly those wherein X is O can react readily with cellulose in the form of



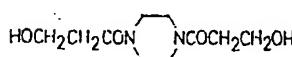
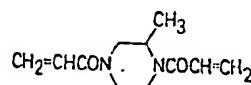
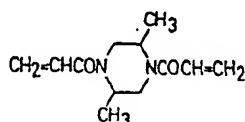
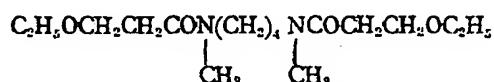
solution, fiber, yarn and fabric and can therefore be used to impart desirable properties to the cellulosic textile and non-textile materials.

Specific examples of compounds coming within the scope of the above formulae include but are not limited to:

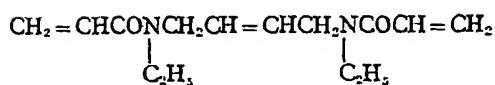
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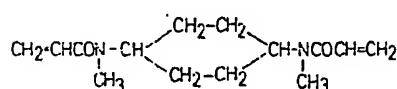
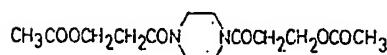
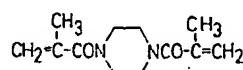
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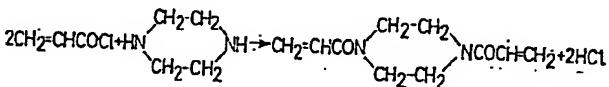


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The compounds of the present invention can be prepared by several means and the choice of the specific process which is employed will depend on the general chemical properties of the specific structures which are desired.

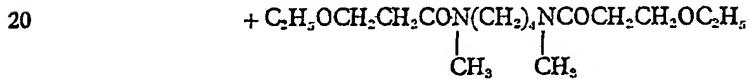
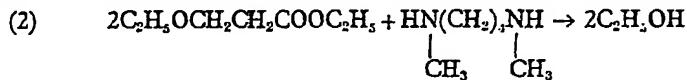
Employing a bis-secondary cyclic amine, an acylation reaction can be carried out with an appropriate acid chloride in the presence of an acid acceptor. This method of preparation is shown in equation (1) below which represents the acylation of piperazine with acryloyl chloride.



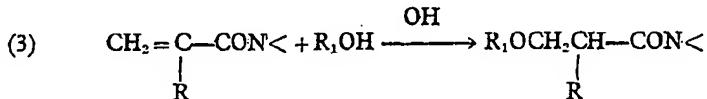
(1)

In a similar manner other amines and other acid chlorides can also be employed in the preparation of correspondingly different final products. For example compounds of the formula $\text{CH}_2=\text{CR.CO.NR}_2\text{NR}_2\text{CO.CR}=\text{CH}_2$ can be obtained by reaction of an acryloyl halide with a hydrazine derivative of the formula $\text{R}_2\text{NH.NH.R}_2$, R_2 having the same meaning as above.

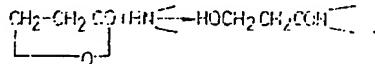
In addition to the acylation-type reactions illustrated above, an aminolysis reaction can be carried out using the esters of a suitable structure. This reaction is shown in equation (2) below wherein $\text{N,N}'\text{-dimethylbutylenediamine 1,4}$ is used as an example of an acyclic bis-secondary amine and ethyl beta-ethoxy propionate is used as an example of a suitable ester.



Unsaturated compounds corresponding to formula I can also be employed to prepare the saturated compounds which correspond to formula III. This is carried out by the addition of alcohols or water as shown in equation (3).



An alternative procedure for preparing compounds wherein R_1 is hydrogen can be carried out by reacting beta-propiolactone with a suitable diamine as shown schematically in equation (3a).

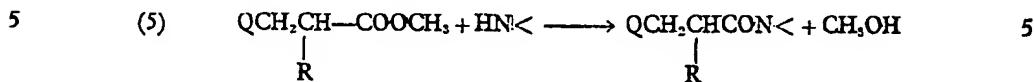
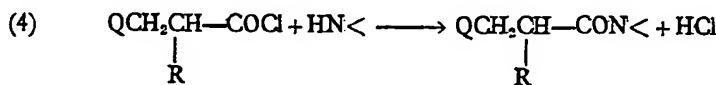


(3a)

A suitable procedure for the preparation of compounds in which R_1 is hydrogen is the reaction of an ester, such as acetate with ammonia, amides or hydrazides as shown schematically in equation (3b):

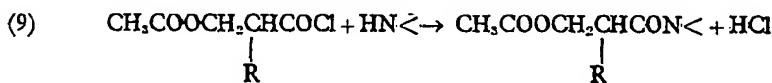
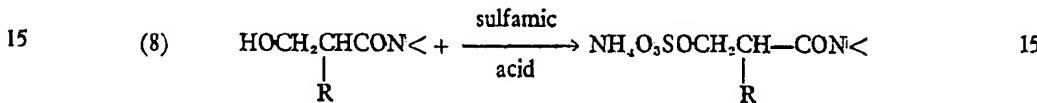
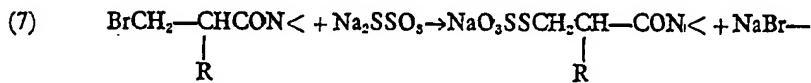
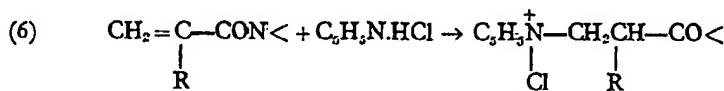


The compounds of the formula II which are saturated amides can be obtained by reaction of an acid halide or ester with a suitable diamine as is shown in equations (4) and (5).



As an alternative procedure the saturated amide compounds can be prepared by adding suitable reagents to the unsaturated amide compounds of Formula I. In addition, these compounds can be prepared from the corresponding beta-halopropionamide compounds as well as other procedures.

10 The compounds of formula II can be prepared by various synthetic procedures depending on the particular reagent chosen. Illustrative of such procedures are equations 6 to 9.



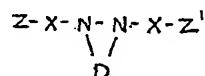
In general, reaction conditions employed in the foregoing preparatory procedures will vary considerably depending on the nature of the starting materials. For example, reactions involving an acid halide in equations (1), (4) and (9) require the use of an acid acceptor to neutralize the acid which is liberated in the course of the reaction. This acid acceptor can be an organic or inorganic base. When an ester is employed as the starting material as illustrated in equations (2) and (5), it is preferable to remove the by-product alcohol which is formed from the reaction mixture by distillation or other suitable means. Any of the reactions described above can be carried out in the presence of a solvent if so desired. In those cases where this procedure is preferred, the solvent should be an inert one. Moderate temperatures are usually employed in the preparation of the unsaturated compounds since these tend to form polymeric by-products if they are subjected to elevated temperatures.

20 25 30 Among the compounds of the present invention are also hydrazine derivatives such as shown in formula IV. Representative compounds of this group are shown below in Table I. In the compounds listed in Table I, X is C=O.

TABLE I
COMPOUNDS OF FORMULA IV

| Z | R ₂ | Z' | Utility |
|--|---------------------|--|--|
| HOCH ₂ CH ₂ | H | HOCH ₂ CH ₂ | Crosslinking agent for polymers containing active hydrogen |
| CH ₃ OCH ₂ CH ₂ | H | CH ₃ OCH ₂ CH ₂ | -do- |
| ClCH ₂ CH ₂ | H | ClCH ₂ CH ₂ | -do- Aldos therapeutic agent |
| C ₆ H ₅ N ⁺ CH ₂ CH ₂ | H | C ₆ H ₅ N ⁺ CH ₂ CH ₂ | -do- |
| CH ₃ OCH ₂ CH ₂ | CH ₃ | CH ₃ OCH ₂ CH ₂ | Crosslinking agent |
| CH ₃ OCH ₂ CH ₂ | H | CH ₃ COOCH ₂ CH ₂ | Unsymmetrical crosslinking agent |
| CH ₃ OCH ₂ CH ₂ | CH ₃ | CH ₂ =CH | Unsymmetrical crosslinking agent |
| C ₂ H ₅ OCH ₂ CH ₂ | -CH ₂ OH | C ₂ H ₅ OCH ₂ CH ₂ | Polyfunctional crosslinking agent |
| NaO ₃ SOCH ₂ CH ₂ | CH ₃ | NaO ₃ SOCH ₂ CH ₂ | - |

Cyclic hydrazine derivatives of the formula



VII.

5 where D is an alkylene or substituted alkylene group of 3 or 4 carbon atoms are also included. Typical compounds are shown in Table II, X is C=O.

5

TABLE II
COMPOUNDS OF FORMULA VII

| Z | D | Z' |
|--|--|--|
| CH ₃ OCH ₂ CH ₂ | -(CH ₂) ₃ - | CH ₃ OCH ₂ CH ₂ |
| -do- | -(CH ₂) ₄ - | -do- |
| -do- | —CH ₂ CH—CH ₂ — OH | -do- |
| HOCH ₂ CH ₂ | —CH—CH ₂ —CH— OH OH | HOCH ₂ CH ₂ |

5 The reactive hydrazide compounds of the present invention can be prepared according to the following description of procedures. For example, compounds of formula IV can be prepared by reacting hydrazine with acylating agents such as the corresponding acid halides, alkyl esters wherein the alkyl group contains from 1 to 5 carbon atoms and anhydrides.

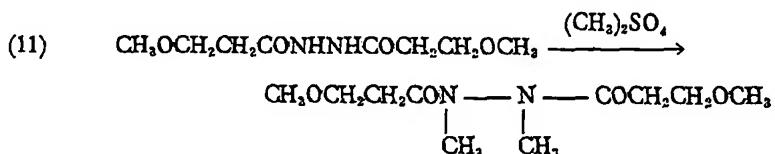
5

Illustrative of this process and employing a compound wherein X is C=O and Z, Z' are both R_1OCH_2CH- , equation (10) shows the acylation of hydrazine with methyl beta-methoxypropionate.



10 The product of equation (10) can be converted to other useful compounds of formulae (IV) and (VII) in which both Z and Z' are $CH_3OCH_2CH_2-$, X is C=O, and R₂ is an alkyl group containing from 1 to 5 carbon atoms, by alkylation reactions as shown by way of example in equation (11) for methylation.

10

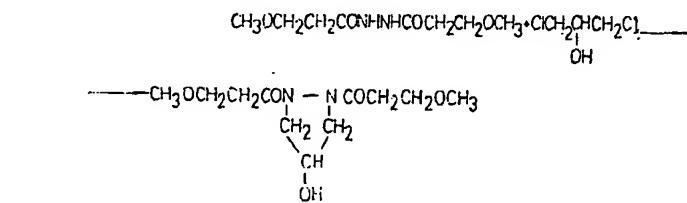


15 By reacting the product of equation (10) with formaldehyde under suitable conditions, a compound will be obtained corresponding to formula IV in which X is C=O, Z and Z' are $CH_3OCH_2CH_2-$ and R₂ is CH_2OH .

15

20 The product of equation (10) can be reacted with an organic dihalide containing 3 or 4 carbon atoms to produce a cyclic derivative such as is shown in Formula VII. For example, equation (12) shows the preparation of a cyclic product from the product of equation (10) and 1,3 dichloropropanol-2.

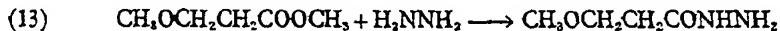
20



(12)

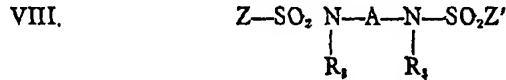
25 Compounds of formulae IV and VII in which Z and Z' are different are obtained by the following procedures. A monoacylated hydrazine can be prepared as shown in equation (13) and converted to unsymmetrical hydrazine derivatives in a subsequent step.

25



30 Among the compounds of the present invention are also polyfunctional sulfonamide derivatives, as shown in formulae V and VI where X = SO_2 . These can be represented by structural formulae VIII and IX.

30

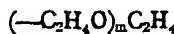




IX.

wherein Z, Z', R₃, A and Y have the meanings previously defined. A particularly suitable group in accordance with formula VIII are compounds wherein A is an alkylene group $-C_nH_{2n}$, n being an integer from 3 to 10, a polyoxyethylene radical

5

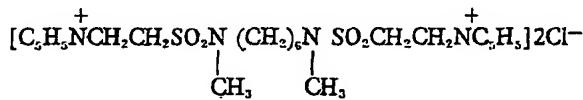
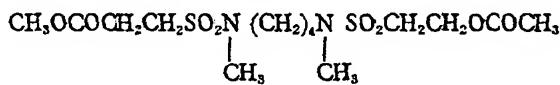


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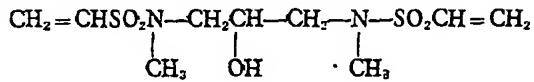
or a polyoxypropylene radical $-(C_3H_6O)_mC_3H_6$, m being an integer from 1 to 20, or a hydroxyalkylene radical $C_nH_{2n-1}(OH)_x$, n being an integer from 3 to 10 and x being an integer from 1 to 4.

10 Representative polyfunctional sulfonamide compounds are shown in Table III. In general, the sulfonamide compounds can be prepared from a suitable sulfonyl chloride and a diamine. 10

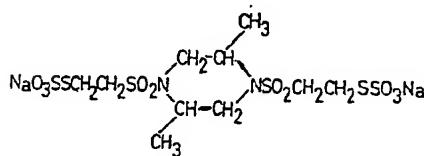
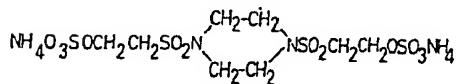
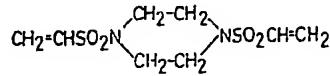
TABLE III.



15

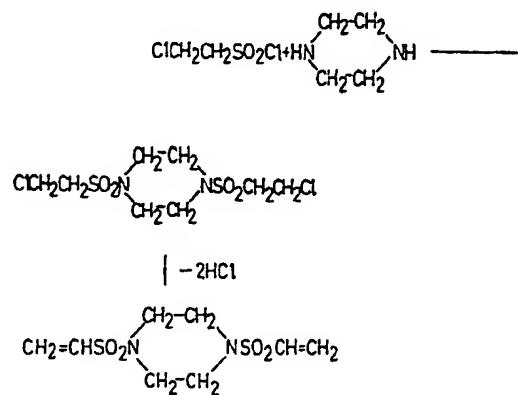


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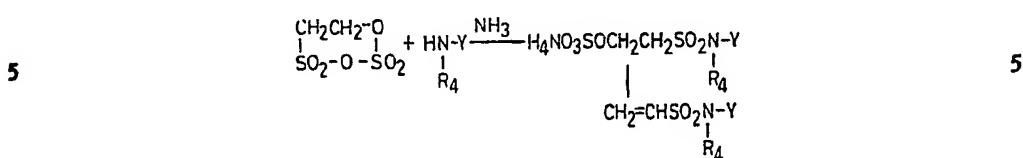


20

Heterocyclic compounds can be prepared by employing a heterocyclic amine as illustrated by equation (14). 20

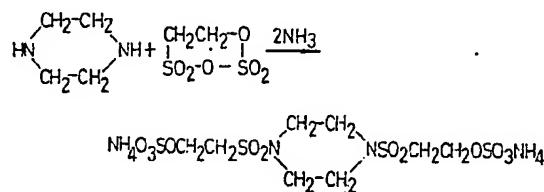


(14) An alternative method for the preparation of these compounds employs carbonyl sulfate as shown in reaction (15):
 (15) Carbonyl sulfate + amine



wherein R₄ is hydrogen or an alkyl group containing from 1 to 5 carbon atoms and Y represents the remainder of the amine molecule.

Illustrative of this reaction is that of piperazine with carbonyl sulfate:

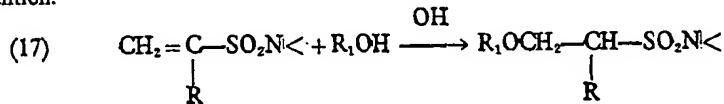


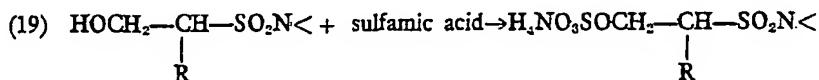
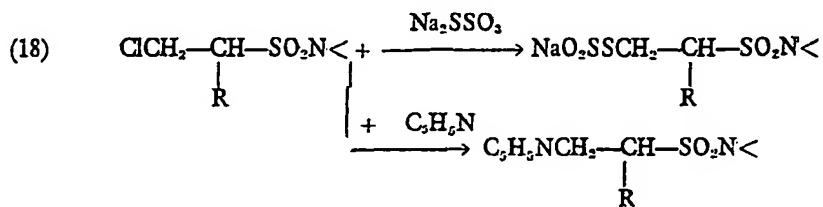
10 (16) In these reactions ammonium hydroxide or other conventional source of ammonia can be used in place of ammonia. 10

15 Although the conditions of reaction employed in the methods of the preparation illustrated above can vary, it is generally preferred that the reaction between the sulfonyl chloride and the amine (equation 14) takes place at a low temperature, usually below 0°C, in the presence of an acid acceptor compound such as a tertiary amine. 15 It is further desirable to employ an inert solvent or diluent in order to aid in cooling the reaction. When the desired monomeric product is unsaturated, a polymerization inhibitor should be used.

20 Reaction (15) takes place under conditions that can be considerably varied. 20 Temperature ranges are not narrowly critical although generally care must be exercised in selecting reaction conditions for specific compounds since the rate of reaction of the amine with the carbonyl sulfate in part depends on the structure of the amine used. Inert solvents may be used for cooling the reaction. Additionally, a polymerization inhibitor is used if the desired product obtained from the reaction is unsaturated.

25 Other methods of preparation can be employed in addition to the direct method by employing a sulfonyl chloride of suitable structure or an amide of suitable structure as illustrated above. For example, the following equations (17) to (19) illustrate some of the reactions that may be used to make the sulfonamide compounds of the present invention. 25





The compounds of the present invention as shown in formulae IV, V, VI are excellent crosslinking agents for polymers containing active hydrogen, and particularly for cellulose.

The properties of cellulosic textile materials, particularly fabrics, can be improved in a desirable manner by reaction of the hydroxyl groups of the cellulose molecule with the novel crosslinking agents of the formulae defined above.

It is known that desirable properties can be imparted to cellulosic material by reaction with polyfunctional compounds capable of reaction with the hydroxyl groups of the cellulose molecules. For example, soluble cellulosic materials can be insolubilized by such crosslinking reactions; the water resistance of cellulosic fibers can be greatly increased; the dimensional stability and crease recovery of fabrics consisting wholly or in part of cellulosic fibers can be greatly enhanced. Thus, many reactants and processes for crosslinking cellulosic materials have been proposed, and some have achieved commercial importance. However, some objectionable aspects which have accompanied many of the prior known reactants and processes have prompted the development of improved processes for crosslinking cellulosic materials, which has been recognized as an important objective, particularly in the textile industry. Crosslinking processes have been widely used for cellulosic textiles in order to improve dimensional stability, resilience, crease recovery, wash/wear properties. Many classes of polyfunctional compounds have been used, including some in which activated olefinic groups react with the hydroxyl groups of the cellulose in an alkali catalyzed reaction.

The polyfunctional amide compounds of the present invention are extremely effective crosslinking agents for cellulosic textiles, and when applied to cellulosic fabrics, yield fabrics possessing outstanding properties of crease recovery, dimensional stability and wash/wear characteristics. Cellulose materials can be crosslinked according to the present invention under mild conditions, thereby essentially avoiding undesirable side reactions such as polymerization and side effects such as degradation of the fibers or discoloration. An added advantage resides in the fact that the chemically modified cellulosic materials are very stable to all conditions encountered in common laundering practices (e.g., alkaline detergents, acid souring, hypochlorite bleaching).

In order to carry out the reaction between the active hydrogen atom-containing polymer (e.g., cellulose) and the polyfunctional amide compounds, the polymer is contacted with the reactant in presence of an alkaline catalyst. Suitable alkaline catalysts are the hydroxides, carbonates, bicarbonates, acetates, phosphates, silicates of alkali metals and ammonium ion. Organic bases can also be employed, and compounds providing a pH above about 7.5 in a 1.0 normal aqueous solution are generally effective. The reaction is driven to substantial completion in a few seconds to a few minutes at temperatures above 200°F and up to about 350°F, although these temperatures can be varied. The temperature of reaction is not critical, and in some cases good yields of the product can be obtained at ambient temperatures in a few hours. The reaction takes place either under anhydrous condition, or in presence of swelling agents for the polymer such as water or ether solvents.

The reactant can be contacted with the polymer by any convenient method, including spraying, coating, padding or dipping. In the case of cellulose textiles, it is preferable to apply the reagent by padding the textile with an aqueous solution thereof.

The reagent and catalyst can be applied simultaneously from the same solution, or they can be applied from separate solutions in any desired sequence of steps.

The concentration of reagent employed in carrying out the process of the present invention can vary within wide limits and is not a critical feature of the invention.

The preferred amount depends on the particular polymer treated, on the structure of the reagent and on the properties desired in the modified polymeric end product. Concentrations of 5 to 25% based on the weight of polymer treated have been found satisfactory.

5 The concentration of alkaline catalyst required to carry out the process of the invention can also be varied and depends on the structure of the reagent as well as on the base strength of the alkaline compound used. In general, amounts from about 0.3% to about 10% by weight based on the weight of the polymer treated have been found to be effective for purposes of the present invention. 5

10 In the treatment of cellulosic textiles according to the new processes, it is often desirable to employ additional finishing agents in order to impart other desirable functional properties. For example, softeners, hand builders, pigments and dyestuffs, stain repellents can be added to the treating solution whenever the mixture containing the added chemicals proves to be sufficiently stable. The addition of chemically inert materials, such as polyethylene, acrylic resins or pigments, does not affect the reaction between the cellulose and the polyfunctional nitrogen-containing compounds. The addition of materials containing reactive groups such as selected dyes or sizing materials to treating solutions containing polyfunctional amides results in a desirable reaction in which the polyfunctional compound acts as a chemical bridge between the cellulose and the added compound. In this manner dyes and sizing compounds can be bonded to cellulose in a durable manner, while simultaneously crosslinking cellulose molecules with the polyfunctional compounds. 10

15 The examples which follow illustrate the outstanding properties of cellulosic textiles treated with the polyfunctional nitrogen-containing compounds of the present invention. For example, symmetrical polyfunctional compounds react readily and efficiently to crosslink cellulose molecules, thereby greatly enhancing resilience and crease recovery. 15

20 The test results shown in the examples were obtained according to the following procedures: 20

25 Crease Recovery — Monsanto Method — AATCC—66—1959
 Tensile Strength — Ravel Strip Method — ASTM D—39—59
 Tear Strength — Elmendorf Method — ASTM D—1424—59
 Shrinkage — AATCC — 96—1960—T 25

30 EXAMPLE I.
 1,4,Bis-(3-Acetoxypropionyl) Piperazine.
 35 A mixture of piperazine (51 g., 0.59 m.), potassium bicarbonate (145 g., 1.45 m.) and water (325 ml.) was cooled to 5° and treated with 3-acetoxypropionyl chloride (199 g., 1.32 m.) added dropwise while maintaining the internal temperature at 4—7°. The addition was complete in 1.5 hrs., and the reaction mixture was then permitted to warm to room temperature with stirring. 35

40 Water (500 ml.) and chloroform (250 ml.) were added to the reaction mixture. The separated aqueous layer was extracted thoroughly with chloroform, and the organic solvent dried and removed to give crude 1,4-bis-(3-acetoxypropionyl) piperazine, (183 g., 90% yield). 40

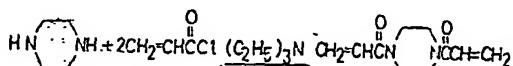
45 Recrystallization from benzene-hexane gave an analytical sample, m.p. 136—138°. 45

| | | | |
|------------|--------|-------|-------|
| Analysis: | C | H | N |
| Calculated | 53.5% | 7.01% | 8.92% |
| Found: | 53.24% | 7.48% | 7.98% |

50 The infrared spectrum (CHCl₃ solution) showed maxima at 5.78 (acetate carbonyl), 6.10 (amide carbonyl), 7.32 (acetate C—CH₃) and 9.65 μ (C—O). 50

Note: In the foregoing and subsequent Examples, all reference to temperature is in degrees C., except as otherwise designated.

EXAMPLE II.
1,4-Diacryloyl Piperazine.



5 Piperazine (60.3 g.) and triethylamine (141.7 g.) were dissolved in chloroform (500 g.) and added dropwise over a two-hour period to a chilled (0°) solution of acryloyl chloride (139.4 g.) in benzene (2500 g.). Vigorous stirring was maintained throughout the addition and for one hour thereafter.

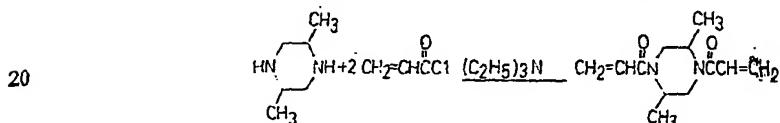
10 Triethylamine hydrochloride (190.6 g.), (expected weight 193 g.) was removed by filtration, and the filtrate concentrated to 1120 g. by evaporation under reduced pressure. The solution was chilled overnight, then filtered to give 1,4-diacryloylpiperazine (68.5 g., 50% yield) as colorless rods, m.p. 93–98°. Its water solubility is at least 35%.

15 Analysis: Percent vinyl by mercaptan addition:

Calculated: 27.8%
Found: 27.5%

A chloroform solution exhibited infrared absorption maxima at 6.10 (vinyl), 6.21 (amide carbonyl), and 10.25 μ (vinyl).

EXAMPLE III.
1,4-Diacryloyl-2,5-Dimethylpiperazine.

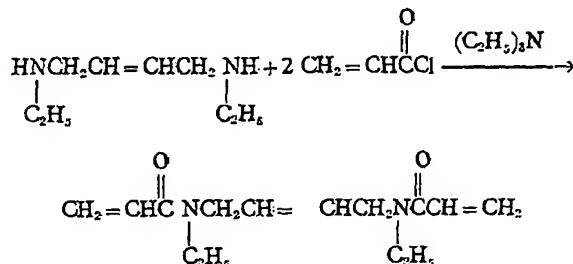


20 1,4-diacryloyl-2,5-dimethyl piperazine was prepared in 40% yield from 2,5-dimethylpiperazine (80% trans—20% cis) by the method described in Example II for the preparation of 1,4-diacryloyl piperazine. The compound was separated by fractional crystallization into two isomers: A, mp 145–151°, and B, mp 83–95°.

25 Analysis (B): Percent vinyl by mercaptan addition:
Calculated 24.3%, Found 23.8%.

A chloroform solution of A exhibited infrared absorption maxima at 6.10 (vinyl), 6.21 (amide carbonyl), 7.24 (C—methyl) and 10.26 μ (vinyl). The infrared spectrum of a chloroform solution of B was nearly identical to that of A.

30 EXAMPLE IV.
 $\text{N},\text{N}'\text{-Diacryloyl-N},\text{N}'\text{-Diethyl-1,4-Diaminobutene-2.}$



35 A solution of $\text{N},\text{N}'\text{-diethyl-1,4-diaminobutene-2}$ (102 g.) and triethylamine (144 g.) in chloroform (500 g.) was added at 0° to a solution of acryloyl chloride (143 g.) and hydroquinone (0.4 g.) in benzene (600 g.). The reaction mixture was stirred 1 hr. at 0°, warmed to room temperature and permitted to stand overnight.

5

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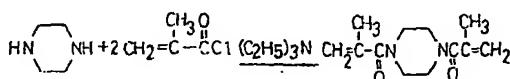
Triethylamine hydrochloride (168 g., expected weight 196 g.) was removed by filtration, and the filtrate evaporated in vacuum to give the crude N,N'-diacryloyl-N,N'-diethyl-1,4-diaminobutene-2 (165 g.).

5 A portion of this crude product was decolorized with charcoal and purified by column adsorption chromatography, using benzene as eluant. The recovered N,N'-diacryloyl-N,N'-diethyl-1,4-diaminobutene-2 obtained in 48% yield was a colorless liquid soluble in an equal weight of water. 5

Analysis: Percent vinyl by mercaptan addition:
Calculated 22.5%, Found 20.6%.

10 A chloroform solution exhibited infrared spectrum adsorption maxima at 6.10 (vinyl), 10
6.22 (amide carbonyl) and 10.25 μ (vinyl).

EXAMPLE V.
1,4-Dimethacryloylpiperazine.



15 Methacryloyl chloride (42 g.) was added at 5° to a solution of piperazine (17 g.), triethylamine (40 g.) and diphenylamine (0.5 g.) in tetrahydrofuran (600 g.). The 15
reaction mixture was maintained at 5—10° for three hours, then permitted to warm to room temperature and stand overnight.

20 Triethylamine hydrochloride (50 g., expected weight 54 g.) was removed by filtration, and the filtrate evaporated to dryness in vacuum. The residue of crude 1,4-dimethacryloylpiperazine (44 g.) melted at 100—104°. 20

A sample, recrystallized from benzene-hexane, melted at 114—116°.

| | Analysis: | Element | Calculated | Found | |
|----|-----------|---------|------------|-------|----|
| 25 | | %C | 64.85 | 64.84 | |
| | | %H | 8.16 | 8.33 | 25 |
| | | %N | 12.6 | 12.51 | |

EXAMPLE VI.

1,4-Bis-(3-Hydroxypropionyl) Piperazine.

30 1,4-bis-(3-acetoxypropionyl) piperazine (158 g., 0.503 m.) was suspended in water (300 ml.) and treated with conc. ammonium hydroxide (29%, 144 g., 1.2 m.). The 30
combined mixture was diluted with ethanol (300 ml.) and stirred for 100 hours.

The solvents were removed in vacuum to leave a solid residue (181 g.) which was taken up in hot chloroform and permitted to crystallize. 1,4-bis-(3-hydroxypropionyl) 35
piperazine, m.p. 123—127° (72.3 g., 62% yield) was isolated by filtration.

35 An analytical sample, m.p. 127.5—129° was prepared by two recrystallizations from chloroform/hexane. The identity of the product was confirmed by the lack of depression of a mixed melting point taken with a sample prepared by the action of beta-propiolactone on piperazine. 35

| | Analysis: | C | H | N | |
|----|------------|--------|-------|--------|----|
| 40 | Calculated | 52.2% | 7.82% | 12.18% | |
| | Found | 52.39% | 8.00% | 12.30% | 40 |

The infrared spectrum (in "NUJOL" [Registered Trade Mark]-refined mineral oil) showed maxima at 2.95 (NH), 6.20 (amide carbonyl), and 9.78 μ (C—O).

EXAMPLE VII.

1,2-Bis-(3-Methoxypropionyl) Hydrazine.

45 Anhydrous hydrazine (133 g., 3.9 m.) was added to methyl 3-methoxy-propionate (1171 g., 9.9 m.) over 45 min. The internal temperature rose to 33° during the first half of the addition. During the second half and for 30 min. afterwards, heat was applied to maintain the internal temperature at 50—60°. The reaction mixture was permitted to cool and stand for 72 hrs. 45

50

The mixture was heated for 11 hrs. at 135°, during which time a distillate (320 g.) of methanol and recovered ester was removed. Finally the rest of the ester was removed in vacuum. The semi-solid residue (635 g.) was dissolved in hot benzene, diluted with hexane and permitted to crystallize.

5 1,2-Bis-(3-methoxypropionyl) hydrazine (204 g., 26% yield) was obtained as white prisms, m.p. 78—83°. A purified sample showed infrared maxima (in CHCl_3) at 3.10 (NH), 6.18 (amide carbonyl), 6.65 (shoulder, amide II band), and 9.0 μ (methoxyl). 5

| 10 | Analysis: | C | H | N | OCH ₃ | 10 |
|----|-----------|------------|--------|--------|------------------|----|
| | | Calculated | 47.05% | 7.89% | 13.72% | |
| | Found | 46.75% | 7.99% | 12.97% | 28.76% | |

EXAMPLE VIII.

1,2-Bis-(3-Acetoxypropionyl) Hydrazine.

15 A mixture of 3-acetoxypropionyl chloride (63 g., 0.42 m.), potassium bicarbonate (42 g., 0.42 m.) and water (100 mL) was chilled to 5° and treated with 85% hydrazine (7.9 g., 0.21 m.) during 10 min. at 5—7°. The reaction mixture was stirred at room temperature for 2 hrs., filtered, and extracted thoroughly with chloroform. 15

20 The solids obtained from the initial filtration and the chloroform extraction (21.6 g., 39% yield) were combined and recrystallized twice from butanol to prepare an analytical sample, m.p. 160—162.6°. 20

| 25 | Analysis: | C | H | N | 25 |
|----|-----------|------------|-------|--------|----|
| | | Calculated | 46.1% | 6.15% | |
| | Found | 47.13% | 6.57% | 11.20% | |

25 The infrared spectrum ("Nujol"—purified mineral oil) showed maxima at 3.15 (NH), 5.80 (acetate carbonyl), and 6.27 μ (amide carbonyl). 25

EXAMPLE IX.

1-(3-Methoxypropionyl)-2-Acryloylhydrazine.

30 1-(3-Methoxypropionyl)-2-(3-chloropropionyl) hydrazine (10 g., 0.048 m.) was suspended in benzene (250 mL) and heated to reflux. Triethylamine (9.7 g., 0.096 m.) was added dropwise to the hot suspension, and the mixture was heated under reflux for eleven hours. 30

35 At the end of the reflux period, the reaction mixture was filtered while hot to remove triethylamine hydrochloride (7.1 g.) and the filtrate permitted to cool slowly. 1-(3-Methoxypropionyl)-2-acryloyl hydrazine (5.7 g., 69% yield), m.p. 104—108°, was isolated by filtration. 35

An analytical sample, m.p. 109—113°, was prepared by recrystallization from benzene/hexane. The purity of this sample was found to be 93% by the activated vinyl method described in THE CHEMISTRY OF ACRYLONITRILE, The American Cyanamid Co., Second Edition, New York, p.61.

| 40 | Analysis: | C | H | N | 40 |
|----|-----------|------------|--------|--------|----|
| | | Calculated | 48.85% | 6.97% | |
| | Found | 49.22% | 7.61% | 16.15% | |

40 The infrared spectrum (CHCl_3) showed maxima at 3.12 (NH), 6.22 (amide carbonyl), 9.01 (methoxyl) and 10.35 μ (vinyl).

EXAMPLE X.

1-(3-Chloropropionyl)-2-(3-Methoxypropionyl) Hydrazine.

45 A mixture of 3-methoxypropionyl hydrazine (139 g., 1.18 m.) and potassium bicarbonate (259 g., 2.59 m.) in water (600 mL) was cooled to 5° and treated with 3-chloropropionyl chloride (300 g., 236 m.) dropwise at 4—7 during one hour. After 50 addition was complete, the reaction was stirred for one hour at room temperature and the product isolated by filtration. Recrystallization from isopropanol gave 1-(3-chloropropionyl)-2-(3-methoxypropionyl) hydrazine (196 g., 74% yield) as fluffy, colorless, needles, m.p. 154—158°.

55 An analytical sample, m.p. 155—158°, was obtained by two further recrystallizations from isopropanol. 55

| Analysis: | C | H | N | Cl |
|------------|--------|-------|--------|--------|
| Calculated | 40.3% | 6.22% | 13.4% | 17.0% |
| Found | 39.92% | 6.17% | 13.01% | 18.37% |

5 The infrared spectrum ("Nujol"—purified mineral oil) showed maxima at 3.10 (NH) (amide carbonyl) and 8.95 μ (methoxyl). 5

EXAMPLE XI.

1-(3-Acetoxypropionyl)-2-(3-Methoxypropionyl) Hydrazine.

10 3-Methoxypropionyl hydrazine (11.8 g., 0.1 m.), potassium bicarbonate (22.4 g., 0.22 m.) and water (100 ml.) were mixed thoroughly and cooled to 4°. 3-Acetoxypropionyl chloride (30 g., 0.2 m.) was added during 30 min. while maintaining the reaction temperature at 4—6°. The mixture was stirred at room temperature for 2 hrs. after the addition was complete, then extracted thoroughly with chloroform. The dried organic extracts were combined, dried, and the solvent removed *in vacuo* to give a solid residue (923 g.). This residue was recrystallized from benzene-hexane to give 15 1-(3-acetoxypropionyl)-2-(3-methoxypropionyl) hydrazine (14.0. g., 60% yield) as colorless rods, m.p. 80—88°.

An analytical sample, m.p. 98—99°, was prepared by two further crystallizations from benzene-hexane.

| Analysis: | C | H | N |
|------------|--------|-------|--------|
| Calculated | 46.50% | 6.90% | 12.05% |
| Found | 46.80% | 6.86% | 12.14% |

The infrared spectrum (CHCl₃) showed maxima at 3.10 (NH), 5.78 (acetate carbonyl), 6.18 (amide carbonyl) and 9.00 μ (methoxyl).

EXAMPLE XII.

1,2-Bis-(3-Methoxypropionyl)-1,2-Bis(Hydroxymethyl) Hydrazine.

25 1,2-Bis-(3-methoxypropionyl) hydrazine (100 g., 0.49 m.) was dissolved in ethyl acetate (500 ml.), brought to pH 8.5 by the addition of 25% methanolic sodium methoxide, and combined with paraformaldehyde (32.3 g., 1.08 m.). The mixture was heated at 50—60° for 2.5 hrs., cooled, filtered, and the ethyl acetate removed *in vacuo* to give a light amber syrup. The formaldehyde content was measured and found to indicate 53% conversion.

30 Re-treatment with paraformaldehyde and base raised the conversion to 87%. This sample was analyzed.

| Analysis: | C | H | N |
|------------|--------|-------|--------|
| Calculated | 45.5% | 7.57% | 10.6% |
| Found | 45.53% | 7.51% | 10.22% |

The infrared spectrum (CHCl₃) showed maxima at 2.98 (OH), 6.03 (amide carbonyl), 9.06 (methoxyl) and 9.70 μ (C—O).

EXAMPLE XIII.

Bis (vinylsulfonyl) piperazine.

40 A solution of 2-chloroethanesulfonyl chloride (136.8 g; 0.84 mole) in 300 ml tetrahydrofuran was slowly added to a stirred solution of recrystallized piperazine (33.6 g; 0.39 mole) and triethylamine (169.5 g; 1.68 mole) in 900 ml of tetrahydrofuran at —70°C over a period of 2.5 hours. The temperature of the mixture was slowly allowed to rise to room temperature and stirring was continued for several hours. The solid was removed by filtration, washed with three 500 ml portions of water and dried. The crude product (53.6 g; 52.6% purity by one hour vinyl analysis (determined by the dodecyl mercaptan method described in the CHEMISTRY OF ACRYLONITRILE, The American Cyanamid Co., Second Ed., N.Y. 1959, p.61) using dodecyl mercaptan method) was recrystallized from acetonitrile and 31.0 g. (29.9% of theory) of product, m.p. 204.0—205.5°C was obtained. The purity of the product by one hour vinyl analysis (dodecyl mercaptan method) was 88%.

EXAMPLE XIV.

1,4-Bis-(vinylsulfonyl)-2,5-dimethyl piperazine.

5 A solution of 2,5-dimethyl piperazine (32.2 g., 0.31 m.; 80% trans—20% cis), triethylamine (131 g., 1.30 m.) and hydroquinone (0.5 g.) in acetone (1000 ml.) was chilled to -10°C . 2-chloroethylsulfonyl chloride (106 g., 0.65 m.) was added to the solution dropwise with vigorous stirring while maintaining the internal temperature at -10 to -15°C . When the addition was complete, the solution was allowed to stir two hours while warming to room temperature and then left overnight.

10 Triethylamine hydrochloride (188 g., calc. 178 g.) was removed by filtration and the filtrate stripped of solvent at reduced pressure. The product was obtained as an oily syrup which was taken up in benzene and crystallized by the addition of hexane. The bis-vinyl sulfonamide was obtained in chunky, colorless crystals, m.p. 145 — 158°C (40.7 g., 44% yield). The infrared spectrum of the product (CHCl_3 solution) showed maxima at 7.48 and 8.72 (SO_2) and 10.32μ (vinyl).

15 This sample was fractionally crystallized from benzene-hexane to give a sparingly soluble isomer A and a more soluble isomer B whose properties are summarized in the table.

| | Isomer | m.p. ($^{\circ}\text{C}$) | Vinyl Analysis ¹ | Dioxane Solubility | |
|----|--------|-----------------------------|-----------------------------|--------------------|----|
| 20 | A | 156—169 $^{\circ}$ | 18.15% | nil | |
| | B | 112—114 $^{\circ}$ | 18.35% | About 30% | 20 |

¹Calculated value: 18.35%. (Determined by the dodecyl mercaptan method described in THE CHEMISTRY OF ACRYLONITRILE, The American Cyanamid Co., Second Ed., N.Y. 1959, p.61).

| | Elemental Analysis % | | | | |
|----|---|-------|------|------|-------|
| | C | H | N | S | |
| 25 | Calculated for $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_4\text{S}_2$ | 40.79 | 6.16 | 9.51 | 21.78 |
| | Found: Isomer A | 40.56 | 7.14 | 9.20 | 21.30 |
| | Found: Isomer B | 40.58 | 6.27 | 9.30 | 21.64 |

EXAMPLE XV.

30 1,4-Bis-(vinylsulfonyl)-2-methylpiperazine.

35 A solution of 2-methylpiperazine (93 g., 0.93 m.) triethylamine (395 g., 3.92 m.) and hydroquinone (3 g.) in acetone (3500 ml.) was chilled to -10°C . 2-chloroethylsulfonyl chloride (319 g., 1.96 m.) was added to the solution dropwise with vigorous stirring while maintaining the internal temperature at -10°C . When the addition was complete, the solution was stirred at -10° for one hour, permitted to warm to room temperature and left overnight.

40 Triethylamine hydrochloride (569 g., calc. 540 g.) was removed by filtration, and the filtrate was stripped of solvent to give the crude bis-vinylsulfonamide (320 g.) as an oily residue. Crystallization from benzene-hexane gave white prisms, m.p. 112— 114°C . (65 g., 25% yield). This sample showed 19.05% vinyl (calc. 19.3%) by the dodecyl mercaptan method. Its infrared spectrum (CHCl_3 solution) showed maxima at 7.45 and 8.70 (SO_2) and 10.32μ (vinyl). A recrystallized sample was submitted for elemental analysis:

| | Anal. | C | H | N | S | |
|----|--------|--------|-------|--------|--------|----|
| 45 | Calc. | 38.56% | 5.75% | 9.99% | 22.80% | |
| | Found: | 38.93% | 6.30% | 10.38% | 24.72% | 45 |

EXAMPLE XVI.

1-(3-methoxypropionyl)-4-(vinylsulfonyl) piperazine.

50 1-(3-methoxypropionyl) piperazine (17.2 g., 0.1 m.) was dissolved in water (250 ml.) containing potassium bicarbonate (22 g., 0.22 m). The solution was cooled to 5°C and 2-chloroethylsulfonyl chloride (17.9 g., 0.11 m.) added dropwise while maintaining the reaction temperature at 2 — 5°C . After the addition was completed, the solution was permitted to stand overnight, then was acidified by the addition of 10% hydrochloric acid (20 ml.). The product was isolated as a light amber syrup by chloroform extraction. Its purity as 87% as determined by vinyl analysis by mercaptan addition.

Its infrared spectrum (CHCl_3 solution) showed maxima at 6.15 (carbonyl), 7.43, 8.70 (sulfone), 9.01 (methoxyl) and $10.4\ \mu$ (vinyl).

| Analysis % | | | | | |
|------------|--------|-------|------|-------|---|
| | Calc. | 45.7 | 6.84 | 10.65 | |
| 5 | Found: | 45.07 | 7.18 | 10.38 | 5 |

EXAMPLE XVII.

Three samples of 80×80 cotton printcloth fabric were padded with aqueous solutions containing 1,4 diacryloyl-2-methyl piperazine (DAMP) and alkaline catalysts in the following proportions:

| | | | |
|----|------------|---|----|
| 10 | Solution A | 15% DAMP + 2% KOH | 10 |
| | Solution B | 15% DAMP + 4% KOH | |
| | Solution C | 15% DAMP + 5% KHCO_3 | |
| | Solution D | 7.5% DAMP + 1% KOH | |
| | Solution F | 7.5% DAMP + 2.5% Na_2CO_3 | |

15 The samples were dried, and subjected to heating under various conditions, as shown in the following Table, then washed. The weight increase due to treatment was determined, and the reaction yield was calculated from the weight increase. The properties of the treated samples are compared with those of an untreated control sample in the Table.

| Sample Treated w. Heating Solution | Conditions | % Yield | (W + F) Crease Recovery | | (W + F) Crease Recovery | |
|--|-----------------|---------|----------------------------|-----|---------------------------------|-----|
| | | | Orig.-Degrees dry | wet | 10 Ldgs.w.bleach-Degrees dry | wet |
| A | Cured 5' 325°F. | 51 | 219 | 240 | 225 | 238 |
| | Steamed 10' | 67 | 228 | 261 | 228 | 263 |
| | Steamed 30' | 77 | 239 | 266 | 238 | 265 |
| B | Cured 5' 325°F. | 55 | 229 | 242 | 219 | 239 |
| | Steamed 10' | 67 | 223 | 250 | 229 | 246 |
| | Steamed 30' | 76 | 228 | 262 | 231 | 256 |
| C | Cured 5' 325°F. | 53 | 219 | 237 | 227 | 237 |
| | Steamed 10' | 70 | 220 | 252 | 226 | 248 |
| | Steamed 30' | 81 | 232 | 265 | 233 | 260 |
| D | Cured 5' 325°F. | 58 | 202 | 227 | 212 | 225 |
| | Steamed 10' | 72 | 237 | 253 | 233 | 252 |
| | Steamed 30' | 100 | 225 | 254 | 206 | 250 |
| F | Cured 5' 325°F. | 59 | 209 | 222 | 208 | 228 |
| | Steamed 10' | 78 | 238 | 242 | 230 | 240 |
| | Steamed 30' | 88 | 249 | 255 | 245 | 252 |
| Untreated Control | | — | 142 | 161 | 146 | 168 |

25 It is apparent from the data shown in the Table that the improvement in crease recovery achieved as a result of treatment is unchanged even after 10 machine launderings at 140°F in presence of a strong chlorine bleaching solution. In addition, the warp tensile strength which, as expected, decreased from 58 lbs. to 40—44 lbs. as a result of the crosslinking treatment, did not decrease further as a result of 10 launderings with chlorine bleach.

EXAMPLE XVIII.

5 A sample of cotton printcloth, padded with the Solution B of Example XVII was rolled smoothly on a coil, covered with a polyethylene sheet and allowed to react at room temperature for 24 hours without drying. The reaction yield obtained under these conditions was 40%, showing that even at room temperature in the presence of 5 water the reaction of DAMP with cotton cellulose proceeds at a significant rate.

EXAMPLE XIX.

10 Samples of 80 x 80 cotton printcloth fabric were padded at 90% wet pickup with aqueous solutions containing 10% diacrylic piperazine (DAP) and alkaline catalysts, dried, heated under various conditions and washed. The weight increase resulting from the treatment determined and the results obtained are summarized in the Table below: 10

| Sample | Catalyst | % Catalyst in Treating Solution | Heating Conditions | % Weight Gain |
|--------|-------------------------------------|---------------------------------|--------------------|---------------|
| A | Benzyl trimethyl ammonium hydroxide | 3 | 3 min. 300°F. | 7.2 |
| B | Benzyl trimethyl ammonium hydroxide | 3 | 3 min. 325°F. | 7.2 |
| C | Benzyl trimethyl ammonium hydroxide | 3 | 3 min. 350°F. | 7.0 |
| D | Benzyl trimethyl ammonium hydroxide | 3 | Steamed 5 min. | 8.3 |
| E | Benzyl trimethyl ammonium hydroxide | 3 | Steamed 10 min. | 8.5 |
| F | KHCO ₃ | 6 | 3 min. 325°F. | 6.7 |
| G | NaOH | 3 | 3 min. 325°F. | 6.3 |

The properties of the treated cotton samples were as follows:

| Sample | W + F Crease Recovery | | Wash/Wear Rating (5L) After Tumble Drying | % Shrinkage After 5 Launderings | |
|-----------|-----------------------|-----|--|------------------------------------|-----|
| | dry | wet | | W | F |
| A | 256 | 244 | 3.8 | 0.0 | 0.5 |
| B | 248 | 246 | 4.0 | 0.5 | 1.0 |
| C | 246 | 261 | 4.5 | 0.5 | 0.5 |
| D | 256 | 258 | 4.5 | 0.0 | 0.5 |
| E | 254 | 271 | 4.8 | 0.5 | 0.5 |
| F | 258 | 255 | 4.5 | 1.0 | 0.5 |
| G | 255 | 246 | 4.0 | 0.0 | 1.0 |
| Untreated | 148 | 164 | 1.0 | 7.0 | 4.5 |

15 The treated samples had excellent appearance and handle. The damage due to retained chlorine was zero for all treated samples. 15

EXAMPLE XX.

The resistance to hydrolysis of fabric samples treated with DAP was outstanding. Samples prepared as described in Example XIX (Sample G) were heated for 3 hours at 140°—150°F. while immersed in acid (0.5 Normal H_2SO_4) and alkaline solutions (0.25 Normal NaOH). After the acid treatment, the crease recovery and the nitrogen content of the sample were unchanged, showing that the crosslinks formed in the reaction were stable to acid hydrolysis even under the severe conditions employed. After the alkali treatment, the crease recovery decreased only very slightly (by about 10 degrees), and the sample retained 80% of the nitrogen content present before the alkaline hydrolysis.

5

10

EXAMPLE XXI.

Four samples of 80 x 80 cotton print cloth were padded with aqueous solutions of alkaline catalysts as shown in the table below and dried. Each sample was then padded with a 12% solution of *1,4 bis vinyl sulfonyl-2 methyl piperazine* in dimethyl formamide at 100% wet pickup, allowed to react under the conditions shown in the table below, and thoroughly washed. The reaction yield obtained and tabulated below was calculated from the nitrogen and sulfur content of the treated samples. The outstanding crease recovery obtained as a result of the treatment is shown in the table.

15

| Sample | Catalyst Solution | Reaction Conditions | % Yield | Crease Recovery W+F | |
|---------|-------------------|-------------------------|---------|------------------------|-----|
| | | | | dry | wet |
| A | 3.8% $KHCO_3$ | Curing 5 min. at 300°F. | 71 | 267 | 250 |
| B | 3.8% $KHCO_3$ | Steaming 5 min. | 95 | 259 | 279 |
| C | 2.6% K_2CO_3 | Curing 5 min. at 300°F. | 72 | 277 | 233 |
| D | 2.6% K_2CO_3 | Steaming 5 min. | 97 | 260 | 271 |
| Control | None | — | — | — | — |

EXAMPLE XXII.

20

The exceptional chemical resistance of the bonds formed in the reaction between cotton cellulose and the bifunctional sulfonamide employed in Example XXI was demonstrated in the following experiment:

A cotton sample was treated with a 2.5% aqueous solution of K_2CO_3 and dried. It was then padded with a 10% solution of the reagent in dimethylformamide, steamed for 5 minutes and washed. The weight increase was 8.0%. The sample was then divided into four portions. One portion was retained as control. The other three were exposed to severe chemical treatments in order to determine the loss in weight and loss in crease recovery, if any, resulting from exposure to acid, alkali and solvent. The results obtained are tabulated below.

25

30

| Treated Sample | Chemical Treatment | % Weight Loss After Chemical Treatment | Crease Recovery | |
|----------------|-------------------------------------|---|-----------------|----------|
| | | | W dry | F wet |
| A | None | — | 244 | 247 |
| B | Refluxing dimethyl formamide 2 hrs. | 0.62 | 242 | 239 |
| C | 0.5N H_2SO_4 3 hrs. at 160°F. | 0.37 | 247 | 260 |
| D | 0.5N NaOH 3 hrs. at 160°F. | 1.22 | 231 | 246 |

It is indeed surprising to find that the stability of the bonds formed to alkaline hydrolysis (Sample D) and to acid hydrolysis (Sample C) is almost equally good.

EXAMPLE XXIII.

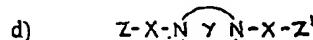
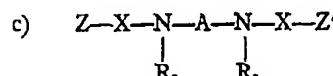
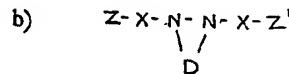
5 Samples of rayon challis fabric were treated as described for cotton samples in Example XXI. Comparable improvements in crease recovery were obtained, and the warp shrinkage of the fabric after 5 launderings at 140°F was found to be only 2.5%, compared to 17.6% for a control sample. 5

10 The foregoing examples illustrate the present invention and it is understood that cellulosic textile materials such as cotton, linen, regenerated cellulose can be treated by the described methods. The cellulosic materials can be treated in the form of loose fibers, mats, non-woven assemblies, yarns and knitted or woven fabrics as well as other forms. Cellulosic textile fabrics and yarns which contain blends of cotton fibers with other natural or synthetic fibers may also be treated according to the present invention. 10

15 Non-cellulosic polymers such as polyvinyl alcohol and starch are further examples of active hydrogen atom-containing polymers that may be chemically modified according to the present invention. 15

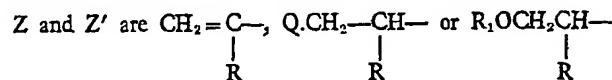
WHAT WE CLAIM IS:—

1. A polyfunctional nitrogen-containing compound having a structural formula falling within one of the following,

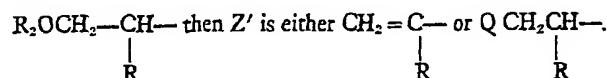


wherein

25 X is $-\text{CO}-$ or $-\text{SO}_2-$ 25
 A is a divalent acyclic aliphatic radical containing at least 3 carbon atoms,
 D is an alkylene or substituted alkylene group containing 3 or 4 carbon atoms,
 R₂ is hydrogen or an alkyl group containing from 1 to 5 carbon atoms or a hydroxy methyl group,
 30 R₃ is an alkyl group containing from 1 to 5 carbon atoms 30



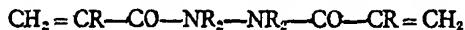
wherein R and R₁ are hydrogen or an alkyl group containing from 1 to 5 carbon atoms and Q is (a) the radical corresponding to a conjugate base of a Lowry-Brønsted acid which has a dissociation constant in water of between 5×10^{-2} and 5×10^{-5} 35 or (b) the residue of a tertiary ammonium cation, and the radical $\begin{array}{c} \text{N} \circledwedge \text{Y} \text{N} \\ | \quad | \\ \circledwedge \quad \circledwedge \end{array}$ is the residue of a cyclic bis-secondary amine, and in formula d) above when Z is 35



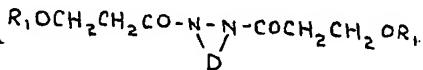
2. A polyfunctional nitrogen-containing compound in accordance with formula a) of claim 1 and having the formula



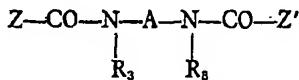
3. A polyfunctional nitrogen-containing compound in accordance with formula a) of claim 1 and having the formula



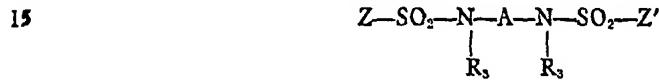
4. A polyfunctional nitrogen-containing compound in accordance with formula b) of claim 1 and having the formula



10 5. A polyfunctional nitrogen-containing compound in accordance with formula c) of claim 1 and having the formula



6. A polyfunctional nitrogen-containing compound in accordance with formula c) of claim 1 and having the formula



wherein A is an alkylene group $-C_nH_{2n-1}$ n being an integer from 3 to 10, a polyoxyethylene radical $-(C_2H_4O)_mC_2H_4$ or a polyoxypropylene radical $-(C_3H_6O)_mC_3H_6$, m being an integer from 1 to 20, or a hydroxyalkylene radical $C_nH_{2n-1}(OH)_x$ n being an integer from 3 to 10 and x being an integer from 1 to 4.

20 7. A polyfunctional nitrogen-containing compound in accordance with formula d) of claim 1 having the formula



8. A polyfunctional nitrogen-containing compound as described in any one of Examples I—XVI.

25 9. A method of making polyfunctional compounds as claimed in claim 2, or 3 which comprises reacting hydrazine or a derivative thereof with an acid halide, an alkyl ester wherein the alkyl group contains from 1 to 5 carbon atoms or an anhydride of an acid.

30 10. A method of making polyfunctional compounds according to claim 9 wherein the halide, ester or anhydride are derived from an acid having the formula



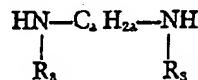
R_1 having the same significance as before.

35 11. A method in accordance with claim 9 wherein polyfunctional compounds as claimed in claim 3 are obtained by reaction of an acryloyl halide with a hydrazine derivative of the formula $R_2NH.NH R_2$, R_2 having the same significance as before.

12. A method of making polyfunctional compounds as claimed in claim 5 or claim 6 which comprises reacting an appropriate acid chloride or ester with an appropriate amine in the presence of an acid acceptor.

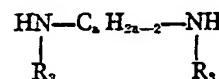
13. A method in accordance with claim 12 for the formation of polyfunctional compounds as claimed in claim 5 which comprises reacting an acid chloride having the formula $Z.CO.Cl$ or an ester having the formula $Z.CO.OR_3$ with an acyclic bis-secondary amine of formula

5

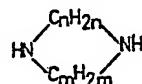


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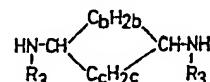
or



where a is an integer from 3 to 10 or with a cyclic bis-secondary amine of formula



or



10

wherein "n" and "m" are integers from 1 to 4 and "b" and "c" are integers of 1 or 2.

10

14. A method in accordance with claim 12 for the formation of polyfunctional compounds as claimed in claim 6 wherein an appropriate amine is reacted with an appropriate sulphonyl chloride or with carbyl sulphate.

15

15. A method in accordance with any of claims 12-14 wherein the reaction is carried out in the presence of an inert solvent.

15

16. A method for the preparation of polyfunctional nitrogen-containing compounds as claimed in claim 1 substantially as described with reference to Examples I to XVI.

20

17. A method of chemically modifying active hydrogen-containing polymers which comprises contacting said polymer under alkaline conditions with a polyfunctional compound as claimed in any of claims 1-8 to effect cross-linking.

20

18. A method in accordance with claim 17 wherein the alkaline conditions are provided by the presence in the reactants of an alkaline catalyst which is a hydroxide, carbonate, bicarbonate, acetate, phosphate, or silicate of an alkali metal or ammonium ion.

25

19. A method in accordance with claim 17 or claim 18 wherein the active hydrogen-containing polymer is a cellulosic textile material or regenerated cellulose.

25

20. A method in accordance with any of claims 17-19 wherein the cellulosic textile material is a fabric containing cotton fibres blended with synthetic fibres.

30

21. A method of chemically modifying active hydrogen-containing polymers substantially as described with reference to Examples XVII to XXIII.

30

22. Chemically modified active hydrogen-containing polymers obtained by any of the processes claimed in claims 17-21.

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